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STRUCTURAL AND SPECTROSCOPIC COMPARISON OF THE COMPLEXES $Cp_2M(PMe_3)(CO)$ (M = Ti, Zr, Hf), $(C_9H_7)_2Ti(PMe_3)(CO)$ AND $Cp_2TiCl(PMe_3)$; X-RAY STRUCTURES OF $Cp_2Ti(PMe_3)(CO)$ AND $Cp_2TiCl(PMe_3)$

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Summary

The photo-induced reaction of $Cp'_2M(CO)_2$ complexes ($Cp' = C_5H_5$, C_9H_7; M = Ti, Zr, Hf) with trimethylphosphine provides the substitution products $Cp'_2M(PMe_3)(CO)$ in high yields. $Cp_2TiCl(PMe_3)$ is obtained by the reduction of Cp_2TiCl_2 with magnesium in the presence of PMe_3. The spectroscopic data for these complexes and the X-ray structures of $Cp_2Ti(PMe_3)(CO)$ and $Cp_2TiCl(PMe_3)$ are compared.

Introduction

It is well-known that acceptor ligands like CO can stabilize titanocene, "Cp_2Ti", and $Cp_2Ti(CO)_2$ (**1**) was reported as early as 1959 [1]. This complex has been widely used as a precursor of titanocene derivatives [2]. Very recently we described the preparation of $Cp_2Ti(PMe_3)_2$ (**2**) [3], a much more reactive and thus more versatile source of "titanocene". Complex **2** loses both phosphine ligands under extremely mild conditions to afford a variety of disubstitution products [3,4]. In some cases, however, **2** is too reactive, causing oligomerization and polymerization of unsaturated ligands such as isonitriles and alkynes. For this reason, we have developed

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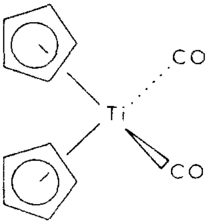
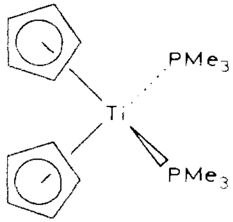
routes to the mixed ligand species $Cp_2M(PMe_3)(CO)$ (M = Ti, Zr, Hf) and some indenyl derivatives and we describe below the syntheses of these complexes and present a comparison of their spectroscopic data. The crystal and molecular structures of the mixed ligand complexes **3** and **7** are also reported, and compared with those of related derivatives. The complexes $Cp_2Ti(PMe_3)(CO)$ (**3**) and $Cp_2Zr(PMe_3)(CO)$ (**4**), obtained under different conditions, have been briefly described previously [5].



(**1**)



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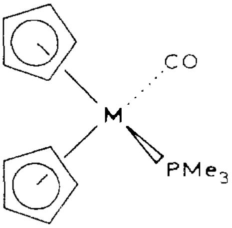
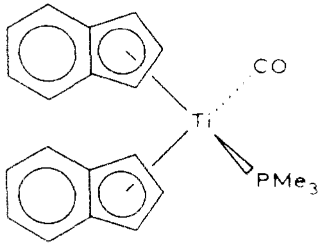
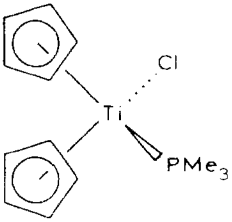


(**3**, M = Ti;
4, M = Zr;
5, M = Hf)



(**6**)



(**7**)

Results and discussion

1. Syntheses

Photochemical replacement of one CO ligand of **1** leads to the mixed derivative $Cp_2Ti(PMe_3)(CO)$ (**3**) in a high yield. It has not been possible to replace the remaining CO ligand to form **2** even under photochemical conditions.

The related compounds $Cp_2Zr(PMe_3)(CO)$ (**4**), $Cp_2Hf(PMe_3)(CO)$ (**5**) and $(C_9H_7)_2Ti(PMe_3)(CO)$ (**6**) (C_9H_7 = indenyl) were also synthesized in good yields by photochemical routes from the respective dicarbonyls. The chloro-substituted complex $Cp_2TiCl(PMe_3)$ (**7**) was obtained via a partial reduction of Cp_2TiCl_2 (**8**) in the presence of PMe_3 and $HgCl_2$. In the absence of $HgCl_2$, reduction is much more rapid, and only **2** is obtained [3]. We also obtained **7** from $(Cp_2TiCl)_2$ and PMe_3 in THF, utilizing the method of Green and Lucas [6].

2. Spectroscopic characterization

The relevant IR and NMR data for compounds **1**–**6** are given in Table 1 together with those for Cp_2TiCl_2 (**8**). The IR spectra reveal a strong interaction between the two-electron ligands CO and PMe_3. Thus, the CO stretching frequencies of **3**–**6** are much lower than those for **1**, as a result of enhanced Ti → CO back-bonding in the mixed ligand systems. A decrease in the CO absorption frequency in the complexes $Cp_2Ti(PMe_3)(CO)$ (**3**), $Cp_2Zr(PMe_3)(CO)$ (**4**) and $Cp_2Hf(PMe_3)(CO)$ (**5**) indicates a strengthening of the M–CO bond on going down the series. Analogous trends have been observed in the corresponding series of complexes $Cp_2M(CO)_2$ (M = Ti, Zr, Hf) [7].

A comparison of the ^1H and ^{13}C NMR spectra of compounds **1**–**3** indicates that the electron density in the cyclopentadienyl rings is very little affected by the substitution of PMe_3 for CO ligands, although it differs considerably from that in the complex Cp_2TiCl_2 (**8**) which is formally titanium(IV). The ^1H and ^{13}C NMR data for the Cp rings in $Cp_2Ti(PMe_3)(CO)$ (**3**), $Cp_2Zr(PMe_3)(CO)$ (**4**) and $Cp_2Hf(PMe_3)(CO)$ (**5**) indicate there is only slight variation in ring electron density

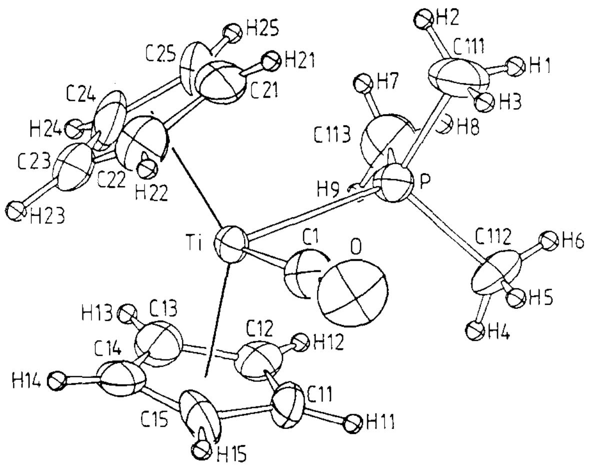


Fig. 1. Molecular structure of $Cp_2Ti(PMe_3)(CO)$ (**3**).

TABLE 1

IR [a] AND NMR [b] SPECTRA OF 1–6

	IR	^{1}H NMR [b]			^{13}C NMR [b]				^{31}P NMR [b,c]
	ν(CO) (cm^{-1})	δ(Cp) (^3J(P,H) in Hz)	δ(Ind)	δ(PMe$_3$) (^2J(P,H) in Hz)	δ(Cp)	δ(Ind)	δ(PMe$_3$) (^1J(P,C) in Hz)	δ(CO) (^2J(P,C) in Hz)	
Cp$_2$Ti(CO)$_2$ (**1**)	1976(A$_1$) 1989(B$_1$)	4.53	–	–	91.9	–	–	260.5	
Cp$_2$Ti(PMe$_3$)$_2$ (**2**) [3]	–	4.51 (2.2)		0.83	91.2		23.6 [d]		+45.2
Cp$_2$Ti(PMe$_3$)(CO) (**3**)	1864(A′)	4.62 (2.6)	–	0.65 (5.6)	91.6	–	20.0 (14.7)	299.0 (3.9)	−29.6
Cp$_2$Zr(PMe$_3$)(CO) (**4**)	1853(A′)	4.91 (1.7)	–	0.74 (5.6)	92.2		21.2 (16.6)	311.1 (2.0)	+10.1
Cp$_2$Hf(PMe$_3$)(CO) (**5**)	1842(A′)	4.78 (2.0)	–	0.89 (5.9)	90.0		22.6 (20.5)	273.2 (2.0)	−5.2
(C$_9$H$_7$)$_2$Ti(PMe$_3$)(CO) (**6**)	1861(A′)	–	6.82m,4.92(d,d) 4.68(br,m)	0.74 (5.6)		123.1, 122.1 96.8, 90.2, 89.1	18.1(d) (13.7)	[e]	+16.1
Cp$_2$TiCl$_2$ (**8**)	–	5.85			119.5				

[a] n-Hexane solution. [b] Toluene-d_8, +20°C. [c] Free PMe$_3$ (in toluene-d_8): δ(PMe$_3$) −58.5 ppm. [d] Spectrum of higher order. [e] Not observed.

TABLE 2

BOND DISTANCES (Å) AND BOND ANGLES (°) OF $Cp_2Ti(PMe_3)(CO)$ (**3**)

Atoms [a]	Distances	Atoms [a]	Angles
Ti-P	2.544(1)	P-Ti-C(1)	88.2(1)
Ti-C(1)	1.963(5)	Z(1)-Ti-Z(2)	136.9(3)
		P-Ti-Z(1)	105.5(2)
P-C(111)	1.826(8)	P-Ti-Z(2)	106.7(2)
P-C(112)	1.824(7)	C(1)-Ti-Z(1)	104.8(2)
P-C(113)	1.826(10)	C(1)-Ti-Z(2)	104.1(3)
C(1)-O	1.185(6)	Ti-P-C(111)	116.6(3)
		Ti-P-C(112)	116.8(3)
Ti-C(11)	2.333(5)	Ti-P-C(113)	118.8(3)
Ti-C(12)	2.371(5)	C(111)-P-C(112)	99.8(4)
Ti-C(13)	2.379(6)	C(112)-P-C(113)	99.4(4)
Ti-C(14)	2.350(6)	C(111)-P-C(113)	102.3(4)
Ti-C(15)	2.335(6)	Ti-C(1)-O	177.2(4)
Ti-C(21)	2.344(6)	C(15)-C(11)-C(12)	107.9(5)
Ti-C(22)	2.345(5)	C(11)-C(12)-C(13)	108.5(5)
Ti-C(23)	2.365(6)	C(12)-C(13)-C(14)	107.9(6)
Ti-C(24)	2.378(7)	C(13)-C(14)-C(15)	109.7(6)
Ti-C(25)	2.367(7)	C(14)-C(15)-C(11)	106.0(6)
		C(25)-C(21)-C(22)	107.2(7)
Ti-Z(1)	2.036(6)	C(21)-C(22)-C(23)	107.6(7)
Ti-Z(2)	2.044(6)	C(22)-C(23)-C(24)	108.1(6)
		C(23)-C(24)-C(25)	108.6(7)
C(11)-C(12)	1.376(9)	C(24)-C(25)-C(21)	108.4(7)
C(12)-C(13)	1.377(8)		
C(13)-C(14)	1.380(9)		
C(14)-C(15)	1.376(11)		
C(15)-C(11)	1.426(8)		
C(21)-C(22)	1.418(9)		
C(22)-C(23)	1.372(12)		
C(23)-C(24)	1.389(11)		
C(24)-C(25)	1.373(11)		
C(25)-C(21)	1.380(13)		

[a] Z(1), Z(2) are the centroids of the C_5 rings.

with changes in the metal. In contrast, the phosphorus nuclei in **3**–**5** experience enhanced shielding proceeding down the series, as evidenced by the ^{31}P NMR shifts. A comparison of the IR data in the complexes $Cp_2Ti(PMe_3)(CO)$ (**3**) and $(C_9H_7)_2Ti(PMe_3(CO)$ (**6**) indicates that substitution of indenyl ligands for Cp ligands has a minimal effect on the electron density of the CO groups.

3. X-Ray structures

A single molecule of $Cp_2Ti(PMe_3)(CO)$ (**3**) is shown in Fig. 1; bond distances and angles are given in Table 2.

The two Cp rings are planar within the error limits, the deviations of the C atoms from the best plane being < 0.003 Å. The vectors normal to the ring planes include an angle of 136.9°.

A single molecule of $Cp_2TiCl(PMe_3)$ (**7**) is shown in Fig. 2; bond distances and angles are given in Table 3.

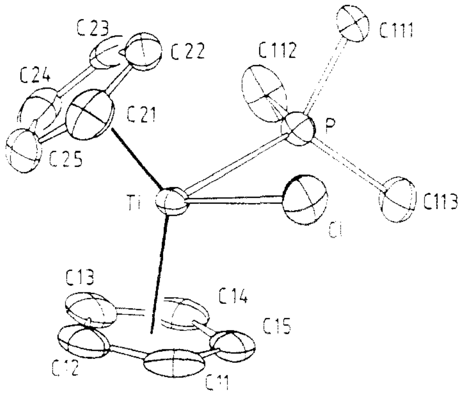


Fig. 2. Molecular structure of $Cp_2TiCl(PMe_3)$ (7).

The two compounds **3** and **7** are isomorphous, with the CO ligand in **3** corresponding to the Cl ligand in **7**. This was indicated by the similar lattice constants for the two compounds and was confirmed by the (independent) structure determina-

TABLE 3

BOND DISTANCES (Å) AND BOND ANGLES (°) OF $Cp_2TiCl(PMe_3)$ (**7**)

Atoms	Distances	Atoms	Angles
Ti–Cl	2.481(2)	P–Ti–Cl	80.4(1)
Ti–P	2.599(1)	Z(1)–Ti–Z(2)	132.3(3)
		P–Ti–Z(1)	107.8(2)
P–C(111)	1.837(5)	P–Ti–Z(2)	105.9(2)
P–C(112)	1.823(6)	Cl–Ti–Z(1)	108.9(2)
P–C(113)	1.835(6)	Cl–Ti–Z(2)	109.2(2)
Ti–C(11)	2.365(6)	Ti–P–C(111)	116.1(2)
Ti–C(12)	2.404(7)	Ti–P–C(112)	117.9(2)
Ti–C(13)	2.374(7)	Ti–P–C(113)	116.3(2)
Ti–C(14)	2.394(8)	C(111)–P–C(112)	100.8(3)
Ti–C(15)	2.372(7)	C(112)–P–C(113)	102.1(3)
Ti–C(21)	2.340(6)	C(111)–P–C(113)	100.8(3)
Ti–C(22)	2.357(7)	C(15)–C(11)–C(12)	107.0(7)
Ti–C(23)	2.383(7)	C(11)–C(12)–C(13)	106.9(6)
Ti–C(24)	2.399(7)	C(12)–C(13)–C(14)	110.5(7)
Ti–C(25)	2.374(6)	C(13)–C(14)–C(15)	107.6(7)
		C(14)–C(15)–C(11)	108.0(7)
Ti–Z(1)	2.071(7)	C(25)–C(21)–C(22)	107.5(6)
Ti–Z(2)	2.064(7)	C(21)–C(22)–C(23)	107.3(6)
		C(22)–C(23)–C(24)	108.2(6)
C(11)–C(12)	1.413(12)	C(23)–C(24)–C(25)	109.5(6)
C(12)–C(13)	1.357(11)	C(24)–C(25)–C(21)	107.4(6)
C(13)–C(14)	1.364(12)		
C(14)–C(15)	1.383(13)		
C(15)–C(11)	1.395(10)		
C(21)–C(22)	1.401(10)		
C(22)–C(23)	1.363(11)		
C(23)–C(24)	1.358(10)		
C(24)–C(25)	1.362(10)		
C(25)–C(21)	1.373(11)		

TABLE 4

BOND DISTANCES AND BOND ANGLES OF 1-3 AND RELATED COMPOUNDS [a]

	Ti-CO	Ti-P	Ti-Z	Ti-Cl	Z-Ti-Z	L-Ti-L	Ref.
$Cp_2Ti(CO)_2$ (**1**)	2.030(11)	-	2.03		138.6	87.9(6)	11
			2.02				
$Cp_2Ti(PMe_3)(CO)$ (**3**)	1.963(5)	2.544(1)	2.04		136.9	88.2(1)	[b]
			2.04				
$Cp_2Ti(PEt_3)(CO)$	2.009(4)	2.585(1)	2.05		138.7	90.3(1)	10
			2.06				
$Cp_2Ti(PMe_3)_2$ (**2**)	-	2.524(4)	2.05		133.2	91.5(2)	3
		2.527(3)	2.06		134.3	92.9(1)	
		2.527(3)	2.06				
$Cp'_2Ti(DMPE)$	-	2.527(4)			135.2(2)	76.9(2)	9
		2.540(4)					
$Cp_2Ti(PF_3)_2$	-	2.340(6)	2.01		137.1	87.3(1)	10
		2.349(6)	2.02		138.0	88.1(2)	
Cp_2TiCl_2 (**8**)	-	-	2.060	2.367(2)	130.89(5)	94.43(6)	19
			2.056	2.361(1)			
$Cp_2TiCl(PMe_3)$ (**7**)	-	2.599(2)	2.071(7)	2.482(2)	132.3(3)	80.4(1)	[b]
			2.064(7)				

[a] Abbreviations: Cp = η^5-cyclopentadienyl (C_5H_5); Cp′ = η^5-methylcyclopentadienyl ($C_5H_4CH_3$), Me = methyl (CH_3), Et = ethyl (C_2H_5), DMPE = 1,2-bis(dimethylphosphino)ethane ($Me_2PCH_2CH_2PMe_2$). Z = center of the C_5 ring (Cp or Cp′); L = ligand other than Cp or Cp′. [b] This work.

tions. An atom at (x, y, z) in **3** has a counter atom at approximately (x, $1/2 - y$, z) in **7**.

In Table 4 the essential structural parameters of a series of Cp_2Ti-type complexes possessing phosphine ligands are tabulated together with those for the related complexes $Cp_2Ti(CO)_2$ (**1**) and Cp_2TiCl_2 (**8**). Comparison of the data indicates that the distance between the metal and the two Cp rings is insensitive to ligand substitution; the Ti–Z values range from 2.01 to 2.07 Å, the complexes with strong acceptor ligands ($Cp_2Ti(PF_3)_2$ and $Cp_2Ti(CO)_2$) having the shortest Ti–Z distances. The Z–Ti–Z angles also vary within narrow limits (130–139°). Hoffmann et al. [8] have predicted that an increase in the π-acceptor character of L should be accompanied by a decrease in the Z–Ti–Z angle. In this series, however, this angle decreases as the π-acceptor CO ligands of **1** are replaced by PMe_3, a poor acceptor, to form **3**, and decrease again in **2**. This is probably due to the steric requirements of PMe_3, which are more important than the expected effects of decreased back-bonding. The structural parameters of the Cp_2Ti unit of the mixed complex $Cp_2Ti(PMe_3)(CO)$ (**3**) fall exactly between those of $Cp_2Ti(CO)_2$ (**1**) and $Cp_2Ti(PMe_3)_2$ (**2**).

The Ti–P distances of all complexes containing trialkylphosphine ligands range from 2.52 to 2.60 Å; the corresponding values of the chelating complex $(MeC_5H_4)_2Ti(dmpe)$ (2.527(4) and 2.540(4) Å) are in good agreement [9]. In contrast, the Ti–P distances of $Cp_2Ti(PF_3)_2$ (2.340(6) and 2.349(6) Å) are much smaller [10], the shortening being due to increased Ti–P back-bonding. Atwood et al. [10] have suggested that the Ti–P bond in $Cp_2Ti(PEt_3)(CO)$ is elongated because of steric crowding. This is supported by a comparison with the Ti–P distance in $Cp_2Ti(PMe_3)(CO)$ (**3**) which is 0.04 Å shorter.

The Ti–C(carbonyl) distance of $Cp_2Ti(PMe_3)(CO)$ (**3**) (1.963(5) Å) is shorter than the corresponding distance in $Cp_2Ti(CO)_2$ (**1**) (2.030(11) Å) [11], presumably because of enhanced Ti → CO back-bonding. This result is consistent with the IR data discussed above.

The L–Ti–L angles (L = CO or phosphine) again fall within a narrow range, from 87.9 to 92.9°. The DMPE complex possesses an exceptionally small P–Ti–P angle (76.9(2)°) as a result of the geometry of the chelating ligand. In the d^0 complex Cp_2TiCl_2 (**8**), the L–Ti–L angle is larger (94.43(6)°) than that of the d^1 complex $Cp_2TiCl(PMe_3)$ (**7**) (80.4(1)°). This is in accord with another of Hoffmann's predictions that as the number of *d* electrons increases, the L–Ti–L angle decreases [8]. The L–Ti–L angles of the d^2 complexes (87.3(1)–92.9(1)°) are actually larger than those in the d^1 complex $Cp_2TiCl(PMe_3)$ (**7**), presumably for steric reason, but are nevertheless smaller than that of Cp_2TiCl_2 (**8**).

Experimental

Preparations

All operations were performed under argon. Pentane and THF were dried over Na/K alloy and freshly distilled. The complexes $Cp_2Ti(CO)_2$ (**1**) [12], $Cp_2Zr(CO)_2$ [7], $Cp_2Hf(CO)_2$ [7] and $Cp_2Ti(PMe_3)_2$ (**2**) [3] were synthesized by literature procedures. Mass spectral values are based on ^{48}Ti, ^{90}Zr and ^{180}Hf isotopes, respectively.

$Cp_2Ti(PMe_3)(CO)$ (3)

A solution of 800 ml pentane containing 5.00 g (21.4 mmol) $Cp_2Ti(CO)_2$ (**1**) and 5.0 ml (53 mmol) PMe_3 was irradiated in a falling-film photo-reactor (Hanovia 450 W) at −20°C. When gas evolution ceased and only the single $\nu(CO)$ absorption of **3** (1864 cm^{-1}) remained in the IR spectrum of the solution, the solvent was removed in vacuo to recover unreacted PMe_3. The residue was extracted with 400 ml pentane and the solution was filtered through filter-aid, concentrated to 100 ml, and cooled to −78°C. Complex **3** formed as dark-brown crystals which were dried in vacuo. Yield 5.35 g (89%). Mass spectrum: *m/e* 254 (M^+ − CO, 8%), 178 (Cp_2Ti^+, 100%), 113 ($CpTi^+$, 37%), 76 (PMe_3, 45%).

$Cp_2Zr(PMe_3)(CO)$ (4)

A solution of 300 ml pentane containing 2.77 g (10.0 mmol) $Cp_2Zr(CO)_2$ and 3.0 ml (32 mmol) PMe_3 was stirred at room temperature and illuminated with room lighting. (The reaction does not proceed in the dark.) When only the single $\nu(CO)$ absorption of **4** remained in the solution IR spectrum (36 h), the solvent was removed. The residue was redissolved in 250 ml pentane and the solution was filtered, concentrated to 50 ml, and cooled to −78°C. Complex **4** was isolated as fine yellow needles. Yield 2.75 g (85%). Mass spectrum: *m/e* 324 (M^+, 13%), 296 (M^+ − CO, 31%), 220 (Cp_2Zr^+, 100%), 76 (PMe_3, 5%).

$Cp_2Hf(PMe_3)(CO)$ (5)

A solution of 20 ml pentane containing 220 mg (0.6 mmol) $Cp_2Hf(CO)_2$ and 0.3 ml (3 mmol) PMe_3 was irradiated at room temperature (Hanovia L 450 W) for 35 min. The orange solution was filtered and removal of the solvent in vacuo left a crystalline orange solid.

Yield 200 mg (81%). Mass spectrum: *m/e* 414 (M^+, 9%), 386 ($M^+ -$ CO, 56%), 76 (PMe_3, 5%).

$(C_9H_7)_2Ti(PMe_3)(CO)$ (6)

A 500 ml Schlenk flask was charged with 1.00 g (2.86 mmol) $(C_9H_7)_2TiCl_2$ [13] and 350 mg (14 mmol) magnesium turnings. THF (50 ml) was added, and the mixture stirred vigorously under a slight CO pressure for 20 h. The solution was then passed through a 3 × 2 cm plug of 10% deactivated alumina and the product was eluted with THF. The solvent was removed in vacuo and the residue was extracted with 200 ml pentane. The extract solution was passed through another 2 × 3 cm plug of 10% deactivated alumina, 2 ml (21 mmol) PMe_3 was added, and the solution was irradiated at −10°C for 2 h. The brown/maroon solution was filtered, and black needles formed as the solvent was removed in vacuo. Yield 590 mg (54%). Mass spectrum: *m/e* 306 ($M^+ - PMe_3$, 3%), 278 (Ind_2Ti^+, 95%), 163 ($IndTi^+$, 20%), 115 (Ind^+, 100%), 76 (PMe_3, 39%), 61($PMe_2{}^+$, 51%).

$Cp_2TiCl(PMe_3)$ (7)

A mixture of 1.00 g (4.02 mmol) Cp_2TiCl_2, 430 mg (17.7 mmol) magnesium turnings, 22 mg (0.08 mmol) $HgCl_2$ and 1.5 ml (16 mmol) PMe_3 in 20 ml THF was stirred at room temperature until the solution became blue. The solvent was removed in vacuo and the residue extracted with toluene. After filtration and concentration in vacuo the solution was cooled to −20°C to give complex **8** as blue-green crystals. Yield 950 mg (82%). Mass spectrum: *m/e* 213 ($M^+ - PMe_3$, 93%), 178 (Cp_2Ti^+, 19%), 148 ($CpTiCl^+$, 100%), 77 (PMe_3H^+, 5%), 65 (Cp^+, 3%).

Spectroscopic measurements

The following instruments were used: IR: Perkin Elmer 297; NMR: JEOL FX 90 Q; Mass: Varian CH 7 (electron impact, 70 eV).

TABLE 5

ATOMIC COORDINATES FOR $Cp_2Ti(CO)(PMe_3)$ (**3**)

Atom	x	y	z	U_{eq}
Ti	0.17122(0)	0.39998(0)	0.31962(1)	0.044(1)
P	0.0718(1)	0.2669(1)	0.3335(1)	0.053(1)
C(111)	0.1138(5)	0.1680(4)	0.4003(8)	0.101(11)
C(112)	−0.0256(4)	0.2827(6)	0.4103(6)	0.079(8)
C(113)	0.0268(6)	0.2205(7)	0.2108(7)	0.103(11)
C(1)	0.1777(3)	0.4008(3)	0.4768(4)	0.069(6)
O	0.1839(3)	0.4043(3)	0.5713(3)	0.115(6)
C(11)	0.0511(3)	0.4863(4)	0.3549(5)	0.069(7)
C(12)	0.0418(3)	0.4572(4)	0.2509(5)	0.063(7)
C(13)	0.1058(4)	0.4936(4)	0.1898(5)	0.077(8)
C(14)	0.1550(4)	0.5462(4)	0.2559(7)	0.078(8)
C(15)	0.1234(4)	0.5435(4)	0.3588(6)	0.080(8)
C(21)	0.2830(4)	0.2987(4)	0.3426(8)	0.091(10)
C(22)	0.3178(3)	0.3856(5)	0.3487(7)	0.090(10)
C(23)	0.3090(3)	0.4243(5)	0.2497(7)	0.082(9)
C(24)	0.2699(4)	0.3632(5)	0.1822(6)	0.089(9)
C(25)	0.2541(4)	0.2868(5)	0.2392(8)	0.092(10)

X-Ray structure of $Cp_2Ti(PMe_3)(CO)$ (3)

The data were collected at 20°C on a Philips PW-1100 diffractometer with graphite crystal monochromated Mo-K_α radiation (λ 0.71069 Å). The crystal fragment had the dimensions 0.3 × 0.3 × 0.5 mm and was sealed in a Lindemann glass capillary.

Crystal data. Orthorhomic, space group *Pbca*, *a* 15.733(2), *b* 15.022(2), *c* 12.475(2) Å, Z = 8; *D*(calc.) 1.271 g cm^{-3}.

Intensity data. $\theta/2\theta$ scans, θ(max) 25°; Lp correction; no absorption correction (μ 6.2 cm^{-1}). 2370 independent reflections; for the following calculations the 1820 reflections with $F_0 > \sigma(F_0)$ were used.

The structure was determined by the Patterson method. All H atoms could be located in ΔF syntheses. Their parameters were also refined. Final *R* indices: $R = 0.064$; $R_w(F) = 0.048$, $w^{-1} = \sigma^2(F) + 0.001F^2$. The maximum of residual electron density was 0.42 eÅ^{-3}. Atomic coordinates are listed in Table 5 [14]. Form factor values for neutral atoms were used [15,16]. Anomalous dispersion terms were from [17]. Program system used: SHELX-76 [18].

X-Ray structure of $Cp_2TiCl(PMe_3)$ (7)

A crystal of dimensions 0.2 × 0.2 × 0.4 mm was sealed in a glass capillary. Data collection was as for **3**.

Crystal data. Orthorhombic, space group *Pbca*, *a* 15.755(a), *b* 14.950(4) *c* 12.217(3) Å, *Z* = 8; *D*(calc.) 1.337 g cm^{-3}.

Intensity data and corrections as for **3**, no absorption correction applied (μ 8.0 cm^{-1}). 2535 independent reflections; for the following calculations the 1962 reflections with $|F_0| > 3\sigma(F_0)$ were used.

The structure was determined by the Patterson method. H atoms were located in ΔF maps. Their contributions to the F_c's were taken into account, but their parameters were not refined. Final *R* indices: $R = 0.066$, $R_w(F) = 0.061$, $w^{-1} =$

TABLE 6

ATOMIC COORDINATES FOR $Cp_2TiCl(PMe_3)$ (7)

Atom	x	y	z	U_{eq}
Ti	0.1753(1)	0.0910(1)	0.3235(1)	0.035(1)
Cl	0.1689(1)	0.0990(1)	0.5261(1)	0.072(1)
P	0.0708(1)	0.2244(1)	0.3455(1)	0.041(1)
C(111)	−0.0250(3)	0.2025(3)	0.4268(4)	0.059(6)
C(112)	0.0245(4)	0.2721(4)	0.2219(4)	0.083(8)
C(113)	0.1125(4)	0.3239(3)	0.4150(5)	0.083(8)
C(11)	0.3223(3)	0.1128(5)	0.3522(6)	0.081(8)
C(12)	0.3153(4)	0.0692(4)	0.2499(8)	0.080(8)
C(13)	0.2733(4)	0.1257(6)	0.1821(5)	0.082(8)
C(14)	0.2567(4)	0.2047(5)	0.2337(7)	0.080(8)
C(15)	0.2862(4)	0.1974(4)	0.3400(7)	0.082(9)
C(21)	0.1314(5)	−0.0577(3)	0.3420(5)	0.073(7)
C(22)	0.0579(4)	−0.0050(4)	0.3457(6)	0.072(7)
C(23)	0.0483(3)	0.0330(4)	0.2450(6)	0.073(8)
C(24)	0.1124(5)	0.0039(4)	0.1799(5)	0.080(8)
C(25)	0.1643(4)	−0.0512(3)	0.2383(6)	0.073(7)

$\sigma^2(F)+0.00006F^2$. The maximum of residual electron density was 0.42 eÅ^{-3}. Atomic coordinates are listed in Table 6. Other details were as for **3**.

Additional data for both structure determinations can be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD 51444, the names of the authors and the journal citation.

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